at a point near the middle of the length of the wall and at a distance up it which is generally about three-quarters of the height. The horizontal gradient for a distance outwards not exceeding 1/10 the height of the wall will not differ by more than 2 per cent. from the normal vertical gradient over a large horizontal area.

On the Enhanced Series of Lines in Spectra of the Alkaline Earths.

By W. M. Hicks, Sc.D., F.R.S.

(Received May 15, 1915.)

The problem of the limits and numerical relations between the lines of the enhanced series of doublets in the alkaline earths has for long been a difficulty to spectroscopists. Ritz* in 1908 gave arrangements for the Sharp series from Mg to Ra inclusive, and proposed series formulæ for Ca, Sr, Ba, in which alone he had three lines from which to calculate the constants. The absence of extra lines rendered it impossible to test his formulæ, but the values of the constants obtained for his formulæ were quite out of line with those of the analogous constants in other series, and produced an instinctive doubt as to whether it gave the correct relation. It is now possible to test his limits by considering whether the denominator differences which give the observed separations have any relation to the oun or not. The result of this consideration is definitely adverse. In none of the three is it possible to make the differences multiples of the oun without supposing observation errors in the doublet separations which are quite inadmissible; and even then in the cases of Ca and Ba by taking odd multiples of δ_1, which is never the case for S doublets in any other known series.

There can be little doubt but that Fowler† has at last settled this question by taking the Rydberg numerator constant to be 4N in place of N, thus combining in one set lines which on the old supposition would be arranged in two series, depending on Sharp and Principal sequences. The object of the present note is the determination of the connection of these series with certain laws which have been arrived at in previous communications‡ to this Society and more especially their dependence on the quantity in (III) called the "oun." This is a quantity peculiar to each element, of magnitude $\delta_1 = 90{\cdot}472w^2$, where w is $1/100$ of the atomic weight. It is convenient to use $\delta = 4\delta_1$ in general. Their values as determined by observation are given in (III, pp. 344–346). The most doubtful is correct to at least 1 in 1000.

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* 'Phys. Zeitschr.,' vol. 16, p. 521.

† 'Phil. Trans.,' A, vol. 214, p. 225 (1914).

‡ 'Phil. Trans.,' A, vol. 210, p. 57 (1909); A, vol. 212, p. 33 (1912); A, vol. 213, p. 323 (1913)—referred to in the following as (I), (II), and (III) respectively.

Fowler gives formulæ for the elements Ca and Sr with the limits for the S, D, and F series and for the S, D series of Mg. These values will be used in what follows. In order to get a conspectus for the whole group I have added a discussion for the corresponding lines in Ba and Ra.

A few preliminary remarks on the series formulæ may not be out of place. In (II, p. 35) I have given reasons that in the triplet series of this group the S series depend on the sequence which in the alkalies give the P_1, and *vice versâ*. If we assume the same result for the doublet series it will be found that the new formulæ reproduce the other lines with much greater closeness than those used by Fowler—who has very naturally taken a Sharp sequence for a Sharp series. The modification consists in taking the constant μ as $1+$fraction or, which comes to the same thing, writing the denominator as $m+\mu+\alpha/(m-1)$. The formulæ on this basis, using the first three lines for data, are

$$\text{Ca} \ldots\ldots \quad n = 70310{\cdot}5 - 4\mathrm{N}/(m+1{\cdot}205860-0{\cdot}065296/m)^2$$
$$\text{Sr} \ldots\ldots \quad n = 64466{\cdot}0 - 4\mathrm{N}/(m+1{\cdot}301682-0{\cdot}081502/m)^2,$$

and the values of O—C, compared with Fowler's, are

Ca	H.......	0	0	0	0·27	0·34
	F.......	−130	0	0	0·3	0·3
Sr	H.......	0	0	0	2·2	
	F.......	−81	0	0	0·7	

In the case of Ba (as allocated below) the formulæ calculated from the second, third, and fourth reproduce the first line with values of $\mathrm{O}-\mathrm{C} = -143$ when $\mu =$ fraction, and 159 when $\mu = 1+$fraction. It is probable that a formula with $m+1+f+\alpha/(m+f)$ would reproduce the lines of each element with very fair accuracy. But the residual errors show that these limits as well as those of Fowler are too large. The cause is probably due to the fact that the first line is not the calculated S(1) but the observed P(1). They never exactly agree.

In the case of D and F series I feel some doubt as to whether the actual lines follow a given formula sequence, although it may be possible that they are in some way related to such typical sequences. There can be little doubt, I think, but that the values of the wave numbers are determined by an expression of the general type $\mathrm{A}-\mathrm{B}/\mathrm{D}^2(m)$ but the denominator certainly cannot itself be a mathematical function of the integer m for both the D_{11} and D_{12} lines, or for both the P_1 and P_2 lines. They are best discussed by calculating the actual values of $D(m)$ from the observed wave numbers, and then attempting to investigate the relationships between them. This is the method adopted in (III) and it will be followed in the present note.

The values of δ for the elements in question are (III, pp. 344–346)

Mg.	Ca.	Sr.	Ba.	Ra.
21·48	58·14	277·89	683·2	1853·16

The theory that the separations of the S, D, and P series depend on multiples of the oun, and that the satellite separations of the D, and consequently the F separations, also depend on other multiples of the same quantity, can, I think, be considered as established, and may be taken as a test for new cases. This part of the discussion will then be taken first.

The exactness of the determination of the denominator differences which produce the observed separations depends almost wholly on the exactness of the separations as measured, and only slightly on the true value of the limit. In fact the value of the difference is affected by the same percentage error as the value of the separation adopted. Any error in the limit produces only a small effect, because it enters as the difference of two numbers each affected by nearly the same errors. To illustrate this point the calculation is given for Ca, and the results only for the other elements.

Fowler quotes for Ca a doublet separation $\nu = 223{\cdot}0$ and limits 70289·2 for S_1 and 70512·2 for S_2. Take the true limits as being ξ greater and that the value of $\nu = 223{\cdot}0$ is affected with an error $d\nu$. Using the numerator 4N, the denominators for these limits are respectively $2{\cdot}498012-17{\cdot}77\xi$ and $2{\cdot}494060-17{\cdot}68\xi$. The difference of these digits, allowing for the error in ν, is, therefore,

$$3952+17{\cdot}7\,d\nu-0{\cdot}09\,\xi.$$

In this $d\nu$ will be less than 0·1, and unless the value of the limit is very much in error the true difference cannot differ from 3952 by more than 2 units in the last place. Now δ for Ca is 58·14, and $68\delta = 3953{\cdot}5$. The possible error in δ is probably much less than one per thousand. These numbers agree easily within any possible observation errors, and we may say that the separation is due to a denominator difference $\Delta' = 68\delta$. In (III), Δ_1, Δ_2, have been used to denote the corresponding values in the triplet series, and Δ for $\Delta_1+\Delta_2$. In order to have a consistent notation we might denote the multiplicity of the series by a corresponding dash and write respectively Δ_1'', Δ_2'', Δ'' for triplets (or two separations) and Δ' for doublets. The same notation might be extended to the series themselves, thus $CaS_1''(3)$ would refer to the triplet system and $CaS_1'(3)$ to the doublets now being considered.

For the other elements Mg, Sr, Fowler's values for $S_1(\infty)$ are respectively 85479·8 with $\nu=91·5$ and 64323·3 with $\nu=800$. But 800 is much too small, and is due to an arithmetical error in deducing the wave number from the wave length 4215·66. The least square value weighted by possible errors is 801·24. Adopting this we have denominator differences

$$\text{for Mg } 1211-13·2\,d\nu-0·02\,\xi, \qquad 56\tfrac{1}{2}\,\delta = 1213,$$
$$\text{for Sr } 16113-20\,d\nu-0·37\,\xi, \qquad 58\,\delta = 16117·7.$$

Hence clearly for Mg $\Delta'=56\frac{1}{2}\delta$ and for Sr $\Delta'=58\delta$, noting that $d\nu$ cannot be more than about 0·1.

Fowler has drawn attention to the difference between the behaviour of Mg and the other elements as showing no line corresponding to negative values in the Diffuse. A similar difference is shown also in the triplet series (III, p. 356), and seems to show that Mg is more analogous to the low melting point elements of this group (Zn, etc.) than to the earths. This difference is exemplified also when the atomic volume term is considered as is done below (p. 462).

Passing on to the second law, the separations of the satellites in the Diffuse series are caused by denominator differences in VD_{11} and VD_{12}. That for the first set is always greater than for succeeding sets, for which latter they are in many cases, though not always, the same. Moreover they are generally multiples of δ_1. The calculated results are here affected by observed errors in the single lines, but again are almost independent of the limit error. The results are of course independent of any formulæ beyond the fact that the wave number is of the form $A-4N/D^2$.

The values of the denominators are given in Table I. The figures in brackets denote possible errors, and as the effect of the change of limit is practically the same for D_{11} and D_{12} it is only entered for the first.

Mg shows no satellites, as is the case also in its triplet series.

The corresponding numbers for Ba and Sr are also placed in this Table from the discussion given below.

In order to obtain the corresponding quantities in Ba and Ra it will be necessary to make a digression to discuss the enhanced series in general in these elements.

Ba.—Ritz gave for the S series the lines —4554·21, —4934·24; 4900·13, 4525·19; 2771·51, 2647·41; to which Saunders* has since added 2287, 2202. The Zeeman effects for the first two pairs have been observed and the

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* 'Phys. Rev.,' vol. 28, p. 152.

Table I.

Ca.

$\Delta' = 3953.$ $\delta = 58\cdot14.$

$2\cdot312876\ (10)-14\cdot2\,\xi$	**858**	$2\cdot312018\ (14)$	$59\,\delta_1 = 857\cdot6$
$47320-29\,\xi$			
$3\cdot360196\ (13)-43\cdot2\,\xi$	**830**	$3\cdot359366\ (13)$	$57\,\delta_1 = 828\cdot5$
$8811-52\,\xi$			
$4\cdot369007\ (?)-95\,\xi$	**799**	$^*4\cdot368208\ (?)$	$55\,\delta_1 = 799\cdot4$
$3972-81\cdot7\,\xi$			
$5\cdot372979\ (?)-176\cdot7\,\xi$			
$5807-120\,\xi$			
$6\cdot378886\ (?)-296\,\xi$			

* Calculated from $D_2-\nu$.

The satellite differences are therefore $59\,\delta_1$, $57\,\delta_1$, $55\,\delta_1$, although, as the third line probably has large observation errors, the $55\,\delta_1$, in spite of its exact agreement with the observed separations, may be 54, 56, or even the same as for the second line. The denominator difference for $m = 5$ and 6 is so excessive as to throw some doubt on the allocation of the last to $D_{11}\,(6)$.

Sr.

$\Delta' = 16117.$ $\delta = 277\cdot89.$

$2\cdot434527\ (12)-16\cdot4\,\xi$	**4587**	$2\cdot429940\ (16)$	$66\,\delta_1 = 4585\cdot0$
$82059-49\cdot5\,\xi$			
$3\cdot516586\ (12)-49\cdot5\,\xi$	**4284**	$3\cdot512302\ (20)$	$62\,\delta_1 = 4307\cdot1$
$23522-57\,\xi$			
$4\cdot540108\ (?)-106\cdot6\,\xi$	**4197**	$4\cdot535911\ (?)$	$60\,\delta_1 = 4168$

The satellite differences are therefore $66\,\delta_1$, $62\,\delta_1$, $60\,\delta_1$. The values for the second and third are not so close as in Ca, but are both within error limits.

Ba.

$\Delta' = 38610.$ $\delta = 683\cdot2.$

$2\cdot421304\ (?)-16\,\xi$	**$14234-0\cdot3\,\xi$**	$2\cdot407070\ (5)$	$83\,\delta_1 = 14176\cdot4$
$148328-35\cdot8\,\xi$			
$3\cdot569632\ (15)-51\cdot8\,\xi$	**$10602-0\cdot4\,\xi$**	$3\cdot559030\ (15)$	$62\,\delta_1 = 10589\cdot6$
$35512-59\,\xi$			
$4\cdot605144\ (80)-111\,\xi$	**$10529-0\cdot5\,\xi$**	$4\cdot594615\ (80)$	$62\,\delta_1$
$17506-91\,\xi$			
$5\cdot622650\ (2000)-202\,\xi$	**8087**	$5\cdot614563\ (2000)$	
18006			
$6\cdot640656\ (?)$			

Ra.

$\Delta' = 112116.$ $\delta = 1853\cdot16+e.$

$2\cdot465091-$	**$35662-$**	$2\cdot429429$	$77\,\delta_1 = 35673$
$146708-$			
$3\cdot611799-$	**$26376-$**	$3\cdot585423$	$57\,\delta_1 = 26407+57\,e$
$58814-$			
$4\cdot670613$			

Zeeman patterns are those for a doublet S series. The doublet separation is 1690·63. There can be no doubt but that the allocation is correct and also that they form an enhanced series. The formula calculated from the 2nd, 3rd, and 4th is

$$n = 58622\cdot8-4\text{N}/(m+0\cdot477659-0\cdot270245/m)^2.$$

This reproduces the first with an error -143. The limit may be taken as probably correct within ±50. The two limits are then $58622\cdot8+\xi$ and 1690·63 additional or $60313\cdot43+\xi$. These give a denominator difference

$$38610-0\cdot98\,\xi+22\cdot35\,d\nu = 56\tfrac{1}{2}\,(683\cdot3-0\cdot01\,\xi+0\cdot4\,d\nu).$$

Now, for Ba, $\delta = 683 \cdot 2$ with an uncertainty of about unity in the fourth digit Hence $\Delta' = 56\frac{1}{2}\delta$.

For the Diffuse series we take the following set—

λ.	n.		
–(10) 5853·91	–17077·96 (0·29)	887·43	1690·59
– 6148·6	–16190·53 (?)		
– 6497·07	–15387·37 (0·24)		
(4) 4166·24	28995·83 (0·29)	205·41	1690·97
(8) 4130·88	24201·24 (0·29)		
(6) 3891·97	25686·80 (0·33)		
(4) 2641·52	37845·97 (0·72)	94·90	1690·66
(8) 2634·91	37940·87 (0·72)		
(5) 2528·60	39536·63 (?)		
2236	44709 (? 10)	40	1680
2234	44749 (? 10)		
2155	46389 (? 11)		
......	....		
2054	48689 (?)		
1987	50312 (?)		

In the first set, the D_{11} line (6148) is taken from an observation by Moore* in the course of his investigation of the Zeeman effect in the Ba spectrum, and it was strong enough to enable him to determine its Zeeman pattern. There can be little doubt as to the allocation of the first two sets, as they both show the Zeeman patterns for diffuse doublets. It is curious, however, that the D_{11} of the first should be so much weaker than the D_{12}, which is abnormally strong. It would seem that only a small proportion of the configurations which give the normal line D_{12} are split up and laterally displaced (III) to the D_{11} set. As a rule they appear to be less stable than those giving D_{11}. It will be seen later that a similar effect is shown by Ra.

In the third set D_{21} (2528) is a line observed by Exner and Haschek. The other lines in the first three sets are measures of Kayser and Runge, whose estimates of possible errors, translated to wave numbers, are inserted in brackets after the measures. The remaining lines are by Saunders (*loc. cit.*). Using the limit for $S(\infty)$ and the second and third lines, the formula for D_{11} is

$$n = 58622 \cdot 8 + 4N/(m + 0 \cdot 711680 - 0 \cdot 426144/m)^2.$$

This gives $\lambda = 2233$ for $m = 5$, which is Saunders' 2234, and $\lambda = 2054 \cdot 5$ for $m = 6$, which establishes the set. The denominators are given in Table I. It is seen that the denominator difference for the first satellite is close on $83\delta_1$, but the difference between $83\delta_1$ and the observed is too large to give so satisfactory a decision as in other cases. This, however, may well be due to the unknown observation error in D_{11}. This line was not observed by Kayser and Runge, but incidentally by Moore in the course of his investigation of the Zeeman phenomenon. The error in D_{12} cannot be larger than 5, and if the whole error be thrown on D_{11} the denominator should be 58 less. Other considerations given below (p. 463) confirm this, and at the same time show that the limit should be about 3 larger. The wave-length of the line should be about 1 Å.U. less than that measured, and make the satellite separation 883·8.

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* 'Ann. d. Phys.,' vol. 25, p. 314.

Ra.—The case of Ra is more difficult as the spectrum has not been measured above 6640 nor below 2700. Moreover, with increasing atomic weight the radiating configurations appear to get more unstable and to break up into numerous others, with the consequent disappearance of regularities. By far the best measurements are those of the spark spectrum by Runge and Precht.* Their plates were not sensitive above 6500. Exner and Haschek observed a few above this. Ritz (*loc. cit.*) gave for the S series the two sets —(100) 3814·578, —(50) 4682·359, and (15) 5813·85, (10) 4533·327. These give doublet separations respectively of 4857·00 and 4857·16. To these may be added for D (3), (20) 4436·489, (50) 4340·830, (50) 3649·748. These selections are probably correct—although we have not their Zeeman patterns as in Ba. They are not sufficient, however, to determine the limits unless a Rydberg formula were exact, in which case the two S lines would be sufficient. But in the other elements limits as thus found are about 1800 too high, and thus quite inadmissible. We are, therefore, driven to apply the method which is used in (III, p. 405) in studying the spectrum of Au. The Rydberg limit from the two S lines is about 57863. From analogy with the other elements the real limit should be about 1800 less, or in the neighbourhood of 56000. It should be such that the value of Δ' required for the observed separation (4857) is a multiple of the oun—of δ_2 from analogy with the others—and that the difference for the satellite separation (496·55) of D(3) should also be a multiple. If the first condition is applied, a series of values for the limits are obtained. Using these, they are tested for the second condition. It is found that one alone satisfies it, and this is then taken as the real limit.

In order to apply this method it is necessary to know beforehand the degree of accuracy of which the data are susceptible. These data are respectively the values of δ, ν, and the satellite separation. For Ra $\delta = 1853{\cdot}16 + e$, where e is probably less than 0·5, or say 1 in 3700. For the other data it is necessary to know the possible errors of observation, which unfortunately Runge and Precht do not give. But they give readings for the special lines in question to the third decimal place (S_1 (3) excepted).

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* 'Ann. d. Phys.,' vol. 14, p. 419.

We shall probably be safe, therefore, in assuming that these are not in error by more than 0·005 Å.U. For $S_1(3)$, which is a good line, we may take 0·05 Å.U. With these the following values of ν are obtained*:—

$$S(2),\ 4857{\cdot}00 - 0{\cdot}034p + 0{\cdot}023q,$$
$$S(3),\ 4857{\cdot}16 - 0{\cdot}147p' + 0{\cdot}024q',$$
$$D(3),\ 4857{\cdot}34 - 0{\cdot}037p'' + 0{\cdot}025q'',$$

in which p and q must lie between ± 1. It is clear that the Diffuse and Sharp separations cannot be exactly the same if our error limits are correctly assumed. Those of S (3) and D (3) may be equal, and as S (2) is possibly really P (1) its smaller ν is in apparent agreement with indications in other series. In any case they do not differ by an amount sufficient to affect the determination of the satellite difference. The $S(\infty)$ will, therefore, be determined by $\nu = 4857{\cdot}05 \pm 0{\cdot}05$.

The satellite separation, with the same supposed observation errors, is $496{\cdot}50 - 0{\cdot}026p + 0{\cdot}025q$, or say $496{\cdot}50 \pm 0{\cdot}05$.

Between 57863 and 55000 nine limits were found which satisfied the first condition. The values of the denominator difference ran from 59δ to 63δ. These were tested on D (3). They all distinctly failed to satisfy the condition except that due to $60\frac{1}{2}\delta$. This belonged to limits 56653·23 and 61510·28. Taking the actual limits to be ξ larger, the denominator difference is $112116 - 2{\cdot}85\xi = 60\frac{1}{2}(1853{\cdot}157 - 0{\cdot}047\xi) = 60\frac{1}{2}\delta$. With the assumed maximum values of e above for δ, ξ can vary only by ± 10. This limit value is now used for D (3), only ξ will be slightly different if the ν for D is 4857·37. The denominators for $D_{11}(3)$ and $D_{12}(3)$ are now 3·611799 and 3·585423. The difference is $26376 - 1{\cdot}2\xi - 262(d\lambda - d\lambda')$, where $d\lambda$, $d\lambda'$, are the errors in observed D_{11} and D_{13}. Now $57\delta_1 = 26407 + 57e$. If these are to be equal $31 + 57e = -1{\cdot}2\xi - 262(d\lambda - d\lambda')$. This equality can be met by values of e, ξ, $d\lambda$, $d\lambda'$ well within their maximum possible errors assumed above. We are justified, therefore, in taking $\Delta' = 60\frac{1}{2}\delta$ and the limit $S_1(\infty) = 56653{\cdot}23$.

The D(2) set of lines should be in reverse order in the red. As no separation 4857 occurs there amongst observed lines, at least $D_2(2)$ is outside the observed region, but it may still happen that the lines $D_{11}(2)$ and $D_{12}(2)$ are within. If so, their denominator difference should be a multiple of δ_1 and their mantissæ considerably less than the corresponding ones for D(3). Also the lines should be strong, and from analogy with the other elements the satellite separation should be rather greater than four times that for D(3). There are two such lines in Runge and Precht's list, viz., (10)5660·81 and (4)6439·1. The latter is very close to the limits of sensitiveness in the red of Runge and Precht's plates, and consequently the line itself must be considerably stronger than is indicated by a plate intensity of 4. Their separation is 2134·61, rather larger than 4×496 and they occupy positions in step with those of Ba. Taking their wave numbers $D_{12} = -17660·51$ and $D_{11} = -15525·90$, their denominators are 2·429429 and 2·465091. Their difference is, therefore, 35662 and $77\delta_1 = 35673 + 19e$, the same within error limits. The ratio for the first and second sets, 77 : 57 = 1·35, is practically the same as for Ba, 83 : 62 = 1·34. Moreover it is noticeable that they show precisely the same abnormality as in Ba, viz., the $D_{11}(2)$ is of less intensity than the satellite $D_{12}(2)$. There is also further evidence in that the denominators of the corresponding lines for $m = 2$ and 3 differ very closely by multiples of δ_1—a result shown by all other known Diffuse series (see III, Table II). Further we should expect F series with a separation 2134·61. Evidence for this is given below.

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* There are several other lines with the same separation, but it will be safer to deal only with the S and D lines.

The set for $m = 4$ will be in the ultra-violet. The shortest lines given by Runge and Precht with $n = 35528·5$ and 36900·7 are strong. But the former gives a denominator with a mantissa smaller than for $m = 3$, and the latter one with a value much higher than analogy with other spectra would lead us to expect. Exner and Haschek give a spark line at 2736·20 with $n = 36547·04$. This gives a denominator 4·670613, with mantissa 58814 above that for $m = 3$, which again is 146708 above that for $m = 2$. It is, therefore, in fair order of magnitude. The difference 58814 should be a multiple of δ_1, but it is affected with an observation error of $1548 d\lambda$. With $d\lambda = 0·05$, this is 77. Now $127\delta_1 = 58828$, and as $\delta_1 = 465·3$, even the large possible error of 77 could not alter the multiple. It is quite possible, therefore, that $\lambda = 2736·20$ is $D_{11}(4)$; the satellite is too faint to have been observed and $D_2(4)$ is outside the region of observation. If, as in Ba, the satellite differences for $m = 3$ and 4 are the same, these unobserved lines would be at 2752·7 and 2428·0, and the satellite separation would be 229·3.

The first three sets of RaD as thus arranged are therefore

λ.	*n.*		
−5660·81	−17660·51	2134·61	4857·00
−6439·1	−15525·90		
−7808·2]	[−12803·51]		
4436·489	22534·16	496·55	4857·34
4340·830	23030·71		
3649·748	27391·50		
[2752·7]	[36317·73]	229·31	4857·00
2736·20	36547·04		
[2428·0]	[41174·73]		

The results obtained for Δ' and the satellite differences are collected in Table II. For purposes of comparison the values of $\Delta = \Delta_1 + \Delta_2$, and of the satellite differences for the triplet series, are also added.

Table II.

	Δ.	Δ'.	Satellites.	
			Triplets.	Doublets.
Mg	$59\,\delta$	$56\frac{1}{2}\,\delta$	None	None.
			Multiples of δ.	Multiples of δ_1.
Ca	$71\frac{1}{2}\,\delta$	$68\,\delta$	$\left\{\begin{array}{lll} 13\,\delta, & 13\,\delta, & 14\,\delta \\ 8\,\delta, & 8\,\delta & \end{array}\right.$	$59\,\delta_1$, $57\,\delta_1$, $55\,\delta_1$
Sr............	$62\frac{1}{2}\,\delta$	$58\,\delta$	$\left\{\begin{array}{lllll} 13\,\delta, & 12\,\delta, & 15\,\delta, & 15\,\delta, & 15\,\delta \\ 8\,\delta, & 8\,\delta, & 8\,\delta, & 8\,\delta & \end{array}\right.$	$66\,\delta_1$, $62\,\delta_1$, $60\,\delta_1$
Ba	$60\frac{1}{2}\,\delta$	$56\frac{1}{2}\,\delta$	$\left\{\begin{array}{ll} 14\,\delta, & 10\,\delta \\ 11\,\delta, & ? \end{array}\right.$	$83\,\delta_1$, $62\,\delta_1$, $62\,\delta_1$
Ra	$68\frac{1}{2}\,\delta$	$60\frac{1}{2}\,\delta$	$\left\{\begin{array}{ll} \frac{1}{2}\,\delta, & \frac{1}{2}\,\delta \\ 2\,\delta & \end{array}\right.$	$77\,\delta_1$, $57\,\delta_1$

In general Δ_1 is a little greater than $2\Delta_2$ and Δ' less than $3\Delta_2$. Thus

	Δ_1.	Δ'.
Mg	$2\,\Delta_2 + 5\,\delta_1$	$3\,\Delta_2 - 5\,\delta_1$
Ca	$2\,\Delta_2 + 4\,\delta_1$	$3\,\Delta_2 - 10\,\delta_1$
Sr	$2\,\Delta_2 + 10\,\delta_1$	$3\,\Delta_2 - 4\,\delta_1$
Ba	$2\,\Delta_2 + 32\,\delta_1$	$3\,\Delta_2 + 16\,\delta_1$
Ra	*$2\,\Delta_2 + 52\,\delta_1$	$3\,\Delta_2 + 20\,\delta_1$

* Δ_2 is doubtful in Ra.

The F Series.—In the F series as given by Fowler the separations are both larger than in the D satellites, for instance 65 as against 59·6 in Ca, and 284·8 as against 279·2 in Sr. The differences are too large and too systematic to be ascribed to observation errors. They seem to be constant for the different orders, which would point to displacements in the limits if they are really the F lines or they are not the normal F lines. Now pairs exist with the proper separation. Again the discussion of the D series has shown that in Ba the F separation should be 887, or more probably 884, and that in Ra, if the suggested values for D_{11}, D_{12} are correct, a separation of 2134 should be expected. These are found, and homologous sets can be found in all four spectra with the true F separations and in which the Zeeman pattern of one of each set (Ra excepted) has been given by Moore (*loc. cit.*) and is the same for the three. But these lines are also closely connected in the same manner in each spectrum with the triplet F series. The clearing up of this connection should probably throw a great deal of light on the connection of the various series, but it will require much further investigation. The discussion is therefore held back for the present. As bearing on the correctness of the identification of the Ra D(2) lines, however, the following lines—in addition to D_{11} and D_{12}—show the separation to be expected.

λ.	*n*.	
4692·1	21306·56	2133·06
4265·1	23439·62	
4740·3	21089·93	2132·45
4305·0	23222·38	2142·94
3941·3	25365·32	

Of these one is probably negative and corresponds to $m = 1$, the other to $m = 2$.

The laws relating to the dependence of the separations of doublets, triplets, and satellites on the oun may be considered so well established that they can be used as tests for new theories. The foregoing discussion thus affords strong testimony in favour of Fowler's explanation. We may now use these new series as tests for certain other relations, which, although perhaps they cannot be considered as proved, yet have a considerable body of evidence in their favour.

(1) We will take as the first of these, the relation that the denominator of the first term of the *p*-sequence—that which in the alkalies gives the P series—is proportional to a multiple of the atomic volume. It would appear that there is in connection with each atom a fundamental quantity, of the nature of a volume. It is roughly proportional (probably to about 2 per cent.) to the atomic volume as measured by the ratio of the atomic weight to the density of the substance in the solid state, a measure which is dependent to some extent on temperature and other effects. The law would state that the mantissa of the denominator of the first line should be kxv, where v is the atomic volume, x a whole number, and k a number in the neighbourhood of 0·002740, this number being probably correct to about 2 per cent. The difficulty in determining its value more accurately depends on the facts that the true value of v is not known within that percentage and to the uncertainty as to whether the fractional part of the denominator itself follows the law, or whether there is some group constant to which the term is added. But, if so, this constant is so near unity that it is quite possible to determine whether the multiple exists—and in that case its value—without ambiguity, allowing the factor to be $0·002740\,(1 \pm 1/50)$.

In the alkalies the *p* sequence gives the P series and consequently

$S_1(\infty) = p_1(1)$, $S_2(\infty) = p_2(1)$. It is easiest, therefore, in this case to apply the test to the limits of the S and D series. It would appear that the p_2 sequence is of a more fundamental type than the p_1, as is also the case in the Diffuse satellites in which the outer satellite is the real normal line from which the more intense D_{11} lines are formed by lateral displacement. Here $p_1(1)$ is formed from $p_2(1)$ by adding Δ. In certain other cases it would appear that the Sharp series depends on the p sequence and the Principal on the s sequence. In this case we look for the presence of the law in VS (2), which is $p(1)$. This is apparently the case in the triplets of Group 2. The values of the multiples for the elements already tested are given in (III, p. 47). In the present case, then, both $S_2(\infty)$ and the VS (2) must be tested. The result is that Mg follows the law in VS (2) and not in $S_2(\infty)$. On the contrary, in Ca, Sr, Ba the law is followed in $S_2(\infty)$ and not for VS (2). The densities used are the same as in (II), viz., Mg (1·72), Ca (1·57), Sr (2·50), Ba (3·77). The results are given in the following table :—

Mg. Mantissa of VS (2) $= \cdot 920434 = \cdot 065050v = \cdot 002710 \times 24v$.
Ca. „ $S_2(\infty) = \cdot 494040 = \cdot 019336v = \cdot 002762 \times 7v$.
Sr. „ „ $= \cdot 595175 = \cdot 016968v = \cdot 002828 \times 6v$.
Ba. „ „ $= \cdot 696694 = \cdot 019110v = \cdot 002730 \times 7v$.
Ra. „ „ $= \cdot 670322 = \cdot 002961\rho v = \cdot 002740xv$.
With density of Ra $= \rho = 0 \cdot 94x$.

The greatest deviation is shown by Sr, in which the density determinations by different observers vary greatly. It is clear that these enhanced series support the truth of the law at least as a first approximation. If Ra is supposed to behave like Ca, Sr, Ba, its density must be $0 \cdot 94x$, where x is an integer. From analogy it would be 6 or 7, giving a density of 5·64 or 6·58. A corresponding theory applied to the triplet series (II, p. 46), in which the numbers are less definite, gave $\rho = 1 \cdot 02x$ with $x = 5$ or 6.

(2) Apparently the Diffuse sequence depends on multiples of the oun in a similar manner to that in which the p sequence depends on the atomic volume. In a very large number of cases the denominator of the outermost satellites of the first set is a multiple of the Δ, and in all other cases the difference between the denominator and the nearest multiple of Δ is itself a multiple of the oun. In the latter case the nature of the evidence for low atomic weights is not decisive as in them the oun is so small that it is easily smothered by observation errors. In the present discussion, then, the question to be tested is whether the first satellite denominator is a multiple of Δ', or differs from such multiple by a multiple of the oun. In the case of Mg the Δ' is too small to settle the question one way or the other.

Ca, using Paschen's value of $\lambda = 8542{\cdot}6$—

For D_{12}, mantissa $= {\cdot}312038\,(10) - 14{\cdot}1\xi = 79\,(3949 - {\cdot}18\xi) = 79\Delta'$, with $\xi = -20$.

Sr, using Randall's value of $\lambda = 9958{\cdot}31$—

For D_{12}, mantissa $= {\cdot}429954\,(?) - 16{\cdot}4\xi$, is not a multiple of Δ'.

For D_{11}, „ $= {\cdot}434527 - 16{\cdot}4\xi = 27\,(16093{\cdot}6 - {\cdot}6\xi) = 27\Delta'$.

If, however, the limit be determined from the second, third, and fourth lines—which is generally to be preferred—it comes out 49 lower. To make the mantissa an exact multiple, the limit should be lower by 32·3, and probably also more correct than $\xi = 0$. It is curious that Sr shows precisely the same kind of displacement in the triplet system, the exact multiple being there found in D_{12} instead of in D_{13}.

Ba.—Here neither D_{11} nor D_{12} give multiples of Δ', but they differ from such by multiples of the oun.

For D_{12}, mantissa $= {\cdot}407070\,(5) - 15{\cdot}9\xi = 11\Delta' - 103\delta_1 - 48 - 16\xi$.

D_{11}, „ $= {\cdot}421304\,(?) - 16\xi = 11\Delta' - 5\delta + 10 - 16\xi$.

Now it was seen above in considering the satellite separations that D_{11} with a large possible error makes the denominator too large by 58. This corrected value would give for D_{11} above

$$\text{Mantissa} = {\cdot}421246 - 16\xi = 11\Delta' - 5\delta - 48 - 16\xi.$$

Ra—

For D_{12}, mantissa $= {\cdot}429429\,(51\,d\lambda) - 16{\cdot}3\xi = 4\Delta' - 41\delta_1 - 36 - 16{\cdot}3\xi$.

D_{11}, „ $= {\cdot}465091\,(41\,d\lambda) - 17\xi = 4\Delta' + 9\delta - 48 - 17\xi$.

With $\xi = -2{\cdot}5$ the relations hold, within small observation errors, for both.

As to the changes in the limits required by the above values of ξ, it is to be noted that for Ba and Ra they should not be large, because if the theory used to determine the Ra limit is correct the value obtained must be close to the real value—and $-2{\cdot}5$ is quite allowable. For Ba the limit is obtained from the second, third, and fourth lines and is a better value therefore than that obtained from the first or fifth. Fowler's limits for Ca and Sr are on the face too large, as the $O-C$ for the later lines show. Hence, here again the evidence of the enhanced series gives weighty support to a relation obtained in (III) from a study of other series.